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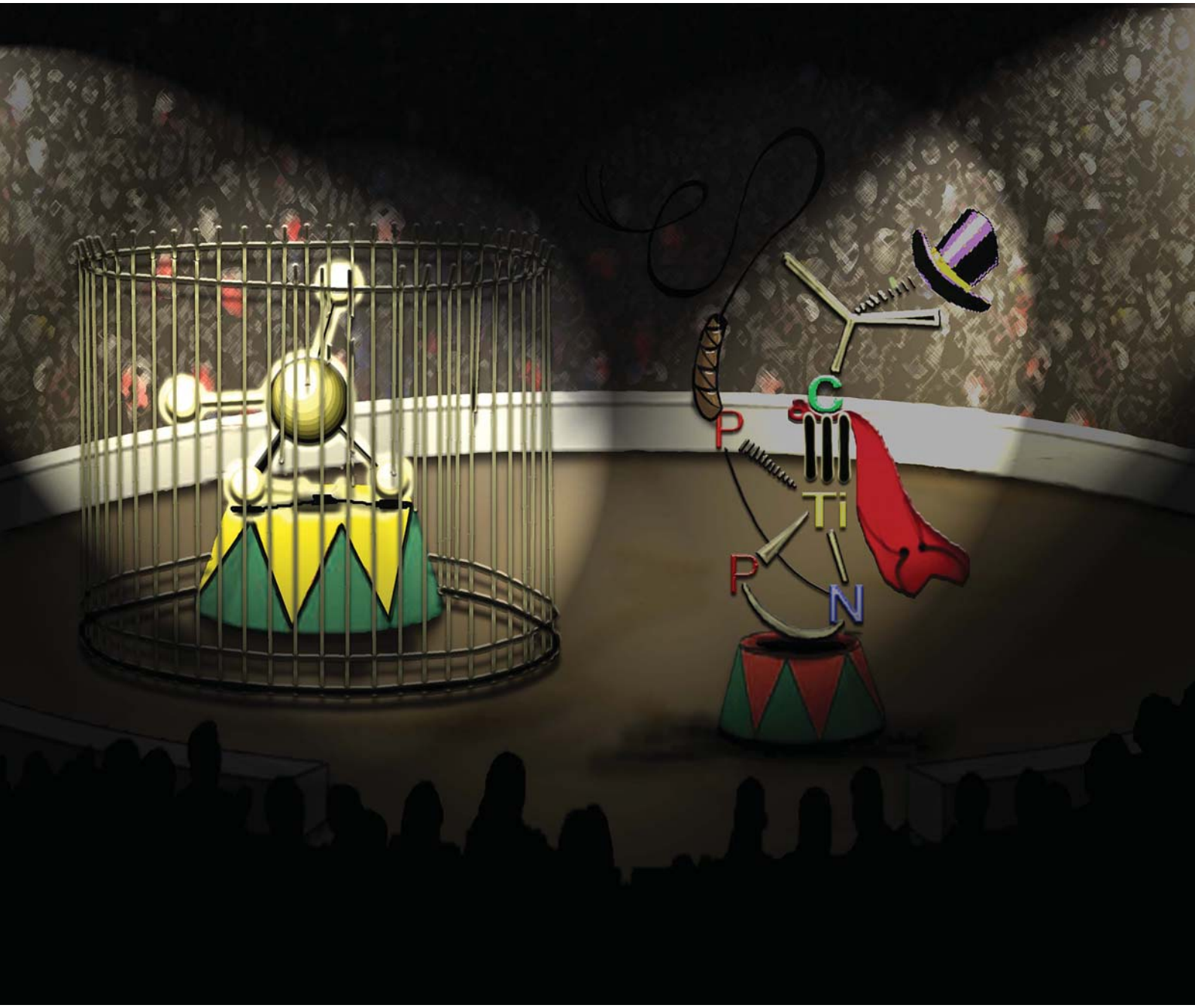

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Methane activation and exchange by titanium-carbon multiple bonds†

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We demonstrate that a titanium-carbon multiple bond, specifically an alkylidyne ligand in the transient complex, (PNP)Ti≡C^{t}Bu (**A**) (PNP$^-$ = N[2-P(CHMe$_2$)$_2$-4-methylphenyl]$_2$), can cleanly activate methane at room temperature with moderately elevated pressures to form (PNP)Ti=CH^{t}Bu(CH$_3$). Isotopic labeling and theoretical studies suggest that the alkylidene and methyl hydrogens exchange, either *via* tautomerization invoking a methylidene complex, (PNP)Ti=CH$_2$(CH$_2^t$Bu), or by forming the methane adduct (PNP)Ti≡C^{t}Bu(CH$_4$). The thermal, fluxional and chemical behavior of (PNP)Ti=CH^{t}Bu(CH$_3$) is also presented in this study.

Introduction

Methane is the most abundant and least reactive of all paraffins, accounting for 70–90% of the vast reserves of natural gas accessible today. With the feedstock of petroleum rapidly dwindling, and the ever-increasing need for energy, a multifaceted approach to the use of cleaner, cheaper, domestic energy sources is required. The exploitation of the intrinsic energy stored in the C–H bonds of methane, a potent greenhouse gas itself, *via* controlled activation and functionalization,[1] represents a quintessential challenge. However, methane's low binding affinity for potential C–H activation and functionalization catalysts in addition to its low reactivity render this substrate untameable for these goals. One strategy towards employing this C_1 feedstock is alkane metathesis,[2–5] where long alkane skeletons are constructed by the combination of C–H bond breaking and C–C bond forming steps. Metal-carbon multiple bonds are thought to play a critical role as reactive intermediates in the aforementioned reactions promoted by solid-state supported Ta, Mo, and W hydrides,[2–6] and are certainly involved in recently discovered homogeneous tandem alkane dehydrogenation/olefin metathesis catalytic systems.[6] Although metal centers carrying methyl ligands have been speculated upon for alkane metathesis catalysts,[5] examples of well-defined homogeneous systems that can dehydrogenate methane[7] in a mechanistically clean fashion remain elusive.[4,8] It is now well established that transition metal alkylidene[9] and alkylidyne[10] complexes can activate aromatic and some aliphatic C–H bonds in an intermolecular manner. Surprisingly, there are no examples of well-defined complexes containing metal-carbon multiple bonds capable of activating the parent alkane, methane, even though metal-imides (M=NR),[11] which can be seen as closely related analogues, are known to show remarkable reactivity towards methane.

In this study we demonstrate that the transient titanium alkylidyne, (PNP)Ti≡C^{t}Bu (PNP$^-$ = N[2-P(CHMe$_2$)$_2$-4-methylphenyl]$_2$),[10] can activate methane at room temperature to form (PNP)Ti=CH^{t}Bu(CH$_3$). Isotopic labelling studies revealed that the Ti-methyl hydrogens in (PNP)Ti=CH^{t}Bu(CH$_3$) exchange with the alkylidene hydrogen thereby suggesting either a tautomerization and/or abstraction pathway to be operative. Theoretical studies also support either pathway with the abstraction route having a slightly lower barrier.

Results and discussion

Methane activation by a titanium neopentylidyne

Previously, we discovered that the alkylidyne precursor (PNP)Ti=CH^{t}Bu(CH$_2^t$Bu) (**1**) can eliminate CH$_3^t$Bu to furnish the transient species (PNP)Ti≡C^{t}Bu (**A**), which can activate benzene to afford (PNP)Ti=CH^{t}Bu(C$_6$H$_5$) (**2**), quantitatively (Scheme 1).[10a,b] In cyclohexane (or C$_6$D$_{12}$) at 31 °C, complex **1** decays with a pseudo first-order rate constant $k = 5.86 \times 10^{-5}$ s^{-1} to myriad products which include CH$_3^t$Bu and cyclohexene (inferred by ^{1}H NMR spectroscopy and GC-MS of the volatiles).[12,13] The same complicated mixture of products is formed when (PNP)Ti=CH^{t}Bu(OTf) (**3**) is treated with Li(cyclo-C$_6$H$_{11}$), therefore suggesting that the putative species (PNP)Ti=CH^{t}Bu (cyclo-C$_6$H$_{11}$), if formed, is unstable under these conditions. Furthermore, at 27 °C complex **1** decays with a $t_{1/2}$ of 3.1 h, independent of whether the solvent is benzene, cyclohexane, hydrofluoroarenes or hydrofluoroalkanes.[10] These results demonstrated the versatility of **A** as a key intermediate, and pointed at its potential for activating C–H bonds. Quantum

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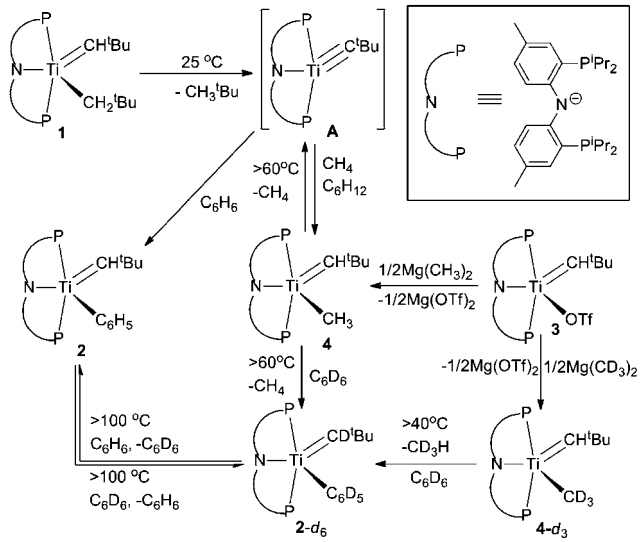


Scheme 1 Methane activation by complex **1** *via* **A** to form **4** as well as other reactivity of **1** and thermal stability of **4** and **4**-d_3.

chemical computer simulations estimated transient **A** to be higher in energy than the precursor **1** by ~5 kcal mol^{-1}[10] and suggested that methane should react with this intermediate under mild conditions. Thus, we hypothesized that methane would be a suitable substrate for reaction with complex **A**.

Exposure of a solution of **1** to CH_4 at a pressure of 310 psi at 31 °C afforded the C–H activation product (PNP)Ti=CH^{t}Bu(CH_3) (**4**) in 54% conversion (based on ^{31}P NMR spectra) after 12 h with k_{avg} = 5.3(5) x 10^{-5} s^{-1} over five independent runs (Fig. 1, Graph A). A similar reaction was observed at 725 psi of CH_4 ($k = 7.2 \times 10^{-5}$ s^{-1}, 50–60% conversion). Interestingly, conversion of **1** to **4** in 95% yield over 12 h could be achieved by increasing the methane pressure to 1150 psi at 31 °C with $k = 7.9 \times 10^{-5}$ s^{-1}. Legzdins observed similar reactivity of the transient butadiene complex, Cp*W(NO)(η^2-CH_2=CHCH=CH_2) with methane at moderately elevated pressures (1025 psi).[14] Therefore, varying the pressure of methane does not inflict any significant change on the pseudo-first order rate of decay of **1** (Fig. 1, Graph B), but it affects the yield of **4**. Deuteration studies with CD_4 at 260 psi verified the formation of the isotopologue, (PNP)Ti=CD^{t}Bu(CD_3) (**4**)-d_4, reaffirming that C–H activation most likely proceeds *via* 1,2-CH bond addition across the alkylidyne ligand of **A**. Moreover, when CD_4 was used, the average rate did not notably deviate from that observed for the activation of CH_4 under similar conditions (k_H/k_D = 1.2(1), 31 °C, Graph A in Fig. 1), thus reasserting that the slow step in the **1** → **4** transformation precedes methane activation.

From our previous experience in C–H activation, we anticipated that deuterating all α-positions in **1**, to form (PNP)Ti=CD^{t}Bu($CD_2{}^t$Bu) (**1**-d_3), should give rise to a KIE of ~4 at 40 °C since α-hydrogen abstraction is expected to be overall rate-determining.[10,12,15] To study the C–H activation step in more detail we prepared the d_1 mixture of isotopomers, (PNP)Ti=CH^{t}Bu(CHD^{t}Bu)/(PNP)Ti=CD^{t}Bu($CH_2{}^t$Bu) (**1**)-d_1 by treating **3**-d_1 with Li$CH_2{}^t$Bu,[10] so as to slow down the rate of decay of the precursor complex and expedite data collection at moderate pressures of CH_4. When **1**-d_1 was exposed to 310 psi of CH_4 pressure, KIE = 2.3 at 31 °C was observed (Fig. 1, Graph A), confirming that the formation of **A**, and not the intermolecular C–H bond activation step of methane, is rate-determining.

Characterization and thermal stability of complex 4

Unlike most organometallic systems that activate methane under mild conditions (<50 °C),[1a,7b–c, 11,14,16] complex **4** is remarkably stable in C_6D_6 at room temperature (rt) with only <5% conversion to **2**-d_6 after six weeks.[13] However, complex **4** extrudes methane in C_6D_6 at 60 °C to form **2**-d_6, but does so slowly with a $t_{1/2}$ of 62.4 h and $k = 3.09 \times 10^{-6}$ s^{-1}. Exploring this reaction over the temperature range 60–90 °C allowed for the extraction of activation parameters $\Delta H^{\ddagger}$ = 29(3) kcal mol^{-1} and $\Delta S^{\ddagger}$ = 0.0 (5) eu (Fig. 2).[13] These parameters suggest an overall similar mechanism for the conversion of **1** to **2**-d_6 but invoke a higher

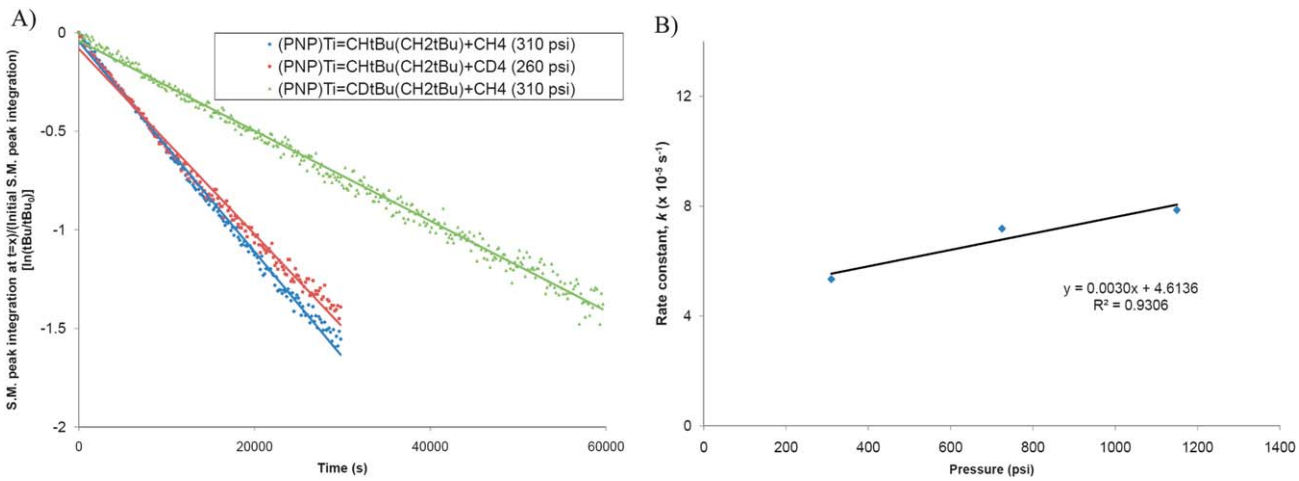


Fig. 1 Kinetic studies for the conversion of **1** to **4** under various pressures of methane. Graph A depicts the pseudo-first order decay of **1** under 310 psi of CH_4 and 260 psi CD_4 as well as decay of **1**-d_1 under 310 psi of CH_4. Graph B shows the dependence of rate on pressure for the conversion of **1** to **4** at 310, 725, and 1150 psi of CH_4.

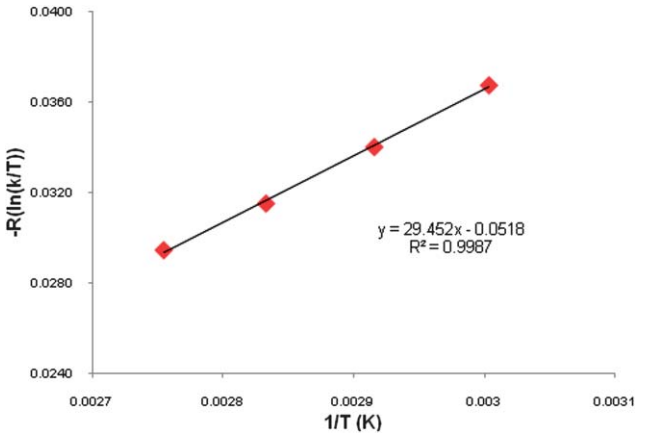
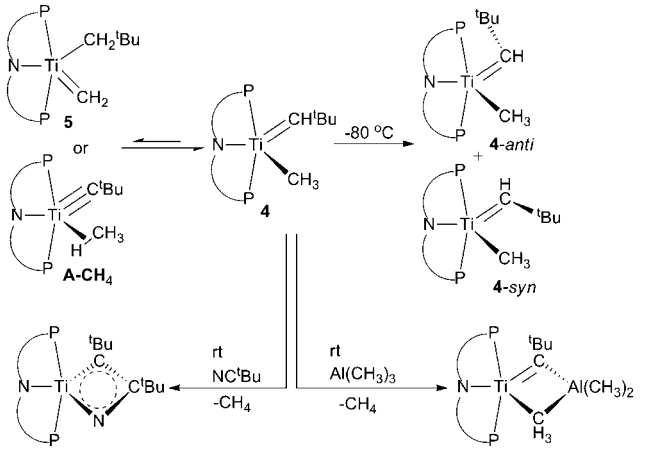


Fig. 2 Eyring plot for the conversion of **4** to **2**-d_6 in C_6D_6 along with a table of rate constants.



Scheme 2 Isomers **4**-*syn* and **4**-*anti* detected at low temperature, tautomerization to the methane adduct **A-CH$_4$**, or methylidene complex **5**, and reactivity showing **4** and not **5** is the resting tautomeric form.

barrier for the formation of **A** ($\Delta G^{\ddagger} \sim 28$ kcal mol^{-1}) given the thermal stability of **4** with respect to **1**.

To confirm our spectroscopic characterization of **4**, we prepared it independently by salt metathesis of **3** with 0.5 equivalents of freshly prepared $Mg(CH_3)_2(OEt_2)_x$ in diethylether, in 97% isolated yield. Diagnostic features of **4** include an alkylidene and methyl resonance at 8.30 and 0.81 ppm, respectively, established by the ^{1}H NMR spectrum collected at rt. The methyl protons (0.81 ppm) exhibit a triplet ($^3J_{HP} = 3$ Hz) due to coupling with the transoid phosphine groups. The phosphine resonances in complex **4** are significantly shifted (32.00 and 21.69 ppm, $^2J_{PP} = 43.9$ Hz) from those observed in **3** or the degenerate alkylidene-alkyl **1** allowing for convenient monitoring of the reaction mixture by ^{31}P NMR spectroscopy. By ^{13}C NMR spectroscopy the alkylidene carbon resonance in **4** is extremely broad at rt. Thus, we conducted variable temperature multinuclear NMR experiments to resolve the ^{13}C NMR spectrum of **4**. Accordingly, the ^{13}C NMR spectrum of **4** at 50 °C displays a more intense signal at 286 ppm (387 Hz) while lowering the temperature of the solution to −80 °C fully resolved this resonance into two distinct peaks, suggesting the presence of two species.[13] By applying a combination of HMQC, 45° DEPT, and ^{1}H-coupled ^{13}C NMR experiments, the alkylidene resonances observed in the ^{13}C NMR spectrum collected at −80 °C (299.2 ppm, doublet, $^1J_{CH} = 96.3$ Hz and 268.8 ppm, doublet, $J_{CH} = 76.2$ Hz), could be readily correlated to the downfield ^{1}H NMR resonances at 8.90 and 7.90 ppm, respectively. As a result, we propose that complex **4** exists as a mixture of alkylidene isomers (also referred to as rotamers), **4**-*anti* and **4**-*syn* (Scheme 2),[17] which isomerize rapidly on the NMR time scale with a low barrier of 10.9 kcal mol^{-1} at −28.9 °C. Variable temperature ^{31}P NMR spectroscopy also corroborate the formation of two isomers of **4**. The ^{31}P NMR spectrum of **4** at −28.9 °C revealed coalescence of the two doublets observed at rt, while further cooling of the NMR solution to −60 °C resolved the broad resonances into two AB couplets, consistent with two distinct C_1 symmetric titanium complexes in approximately 3 : 2 ratio. Increasing the temperature to rt regenerated the original "averaged" AB set, indicating rapid chemical Ti=C bond rotation with respect to the NMR time scale. Therefore, complex **4**, which can be derived from methane activation, exist as a mixture of alkylidene rotamers at rt.

We have found that complex **4** behaves like an alkylidyne synthon analogous to **1**. The treatment of **4** with $Al(CH_3)_3$ generated the known neopentylidyne-zwitterion (PNP)Ti(μ_2-C^{t}Bu)(μ_2-CH$_3$)(AlMe$_2$)[18] concurrent with CH_4 elimination. Likewise, the neopentylidyne functionality can also be trapped with NC^{t}Bu to render the azametallacyclobutadiene complex (PNP)Ti(C^{t}BuC^{t}BuN)[19] along with release of CH_4 (Scheme 2). Both complexes were generated quantitatively as established by ^{31}P NMR spectroscopy as well as isolated in yields exceeding 70% without evidence of formation of another species.

Proton exchange in complex 4

In order to elucidate the dynamics of the alkyl and alkylidene ligands in **4**, isotopic labelling experiments were performed by independently preparing the isotopologues (PNP)Ti=CD^{t}Bu(CH$_3$) (**4**)-d_1, (PNP)Ti=CH^{t}Bu(CD$_3$) (**4**)-d_3, and (PNP)Ti=CD^{t}Bu(CD$_3$) (**4**)-d_4.[13] Complex **4**-d_1 eliminates CDH_3 more slowly than **4** extrudes CH_4 in a C_6D_6 solution (KIE = 1.79, 80 °C) to cleanly produce compound **2**-d_6 (Scheme 1). Since **4**-d_1 extrudes CDH_3 slowly at temperatures exceeding 60 °C, it provided us with a window of $\Delta T \sim 33$ °C to examine if such *d*-exchange is possible at the α-carbons. Mild thermolysis of **4**-d_1 in C_6D_6 over 4 days at 40 °C slowly gave rise to proton incorporation at the neopentylidene α-C to form the isotopomer (PNP)Ti=CH^{t}Bu(CDH$_2$). This suggests that the α-hydrogens of the methyl and alkylidene ligands in **4** must be exchanging.[13,20] Fig. 3 depicts stacked ^{1}H NMR spectra of the expanded aryl region of **4**-d_1 in C_6D_6 (80 °C), which highlights proton-inclusion at the alkylidene position. In addition, the slow background reaction involving elimination of CDH_3 concurrent with formation of **2**-d_6 at the expense of the decay of **4**-d_1 is observed. The exchange of **4**-d_1 to (PNP)Ti=CH^{t}Bu(CDH$_2$) is not only slow but reversible since we also observe deuterium exchange in the isotopologue **4**-d_3 after 4 days at 40 °C in C_6D_6 – in addition to formation of some **2**-d_6 and CHD_3 by ^{1}H and ^{2}D NMR spectroscopy.[13] Inadvertently, the exchange in **4**-d_3 in

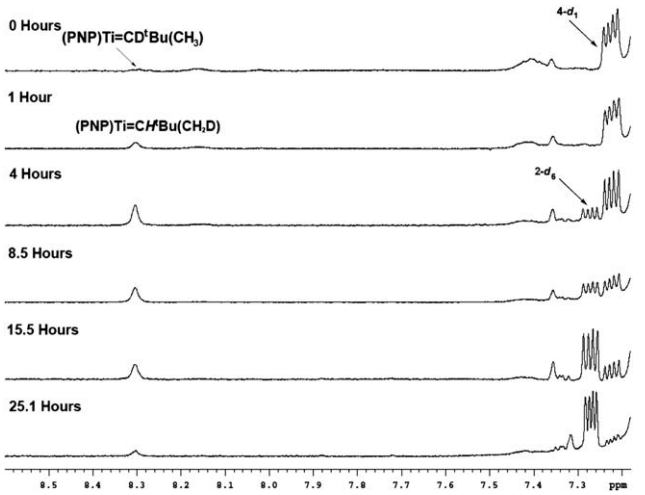


Fig. 3 ^{1}H NMR spectra at low field region for the thermolysis of (PNP)Ti=CD^{t}Bu(CH$_3$) in C_6D_6 at 80 °C.

C_6D_6 is slow and thus overshadowed by α-hydrogen abstraction (CHD_3 elimination) given that the rate of conversion to **2**-d_6 at 80 °C is very close to the rate of conversion of **4** to **2**-d_6 (KIE = 1.01).

To corroborate that exchange does take place in **4**, the rate of decay of **4**-d_4 to **2**-d_6 in C_6D_6 was also measured. The KIE is higher than that observed for **4**-d_1 (KIE = 2.06, 80 °C). The difference in rate constants between **4**-d_1 and **4**-d_4 must arise from hydrogen exchange (*vide infra*). As a result of our studies, we propose the exchange phenomenon in complex **4** to occur *via* a tautomerization, meaning formation of a methylidene complex (PNP)Ti=CH_2(CH_2^{t}Bu) (**5**), or by abstraction/addition *via* the methane adduct (PNP)Ti≡C^{t}Bu(CH_4), **A-CH$_4$** (Scheme 2). Our previous work established that the α-hydrogens in (PNP)Ti=CH^{t}Bu(CD_2^{t}Bu) can rapidly exchange at room temperature to a mixture of isotopomers **1**-d_2 (1 : 2 ratio), so the proposed exchange observed here is not completely unexpected.[10,12]

Theoretical studies of the proton exchange in complex 4

Density functional theoretical analysis suggests that the activation energies of the α-hydrogen abstraction and tautomerization routes are energetically similar, with the former being 33 and the latter 36 kcal mol^{-1}. Fig. 4 depicts these two most probable pathways of reaction for complex **4**, illustrating that **4** is significantly lower in solution-phase free energy than its tautomeric methylidene complex **5**, which lies about 8 kcal mol^{-1} higher in energy than **4**, but 10 kcal mol^{-1} below the transient alkylidyne **A** and 18 kcal mol^{-1} below **A-CH$_4$**. In addition to paths a and b having similar rate determining barriers, **4-TS$_a$** and **4-TS$_b$**, Fig. 4 more clearly depicts how isotopologues **4**-d_1 and **4**-d_3 increase the energies of **4-TS$_b$** and **4-TS$_a$**, respectively.

At present, we propose part of the difference in energy between **4** and **5** to be imposed by an α-agostic interaction present in the neopentylidene (and absent in the methylidene). This type of interaction can account for 1–10 kcal mol^{-1}, which could explain a difference in energy of 8 kcal mol^{-1}. In fact, the computed Ti–C–H angles of 118.5° and 129.7° and H–C–H angle of 111.8° in **5**

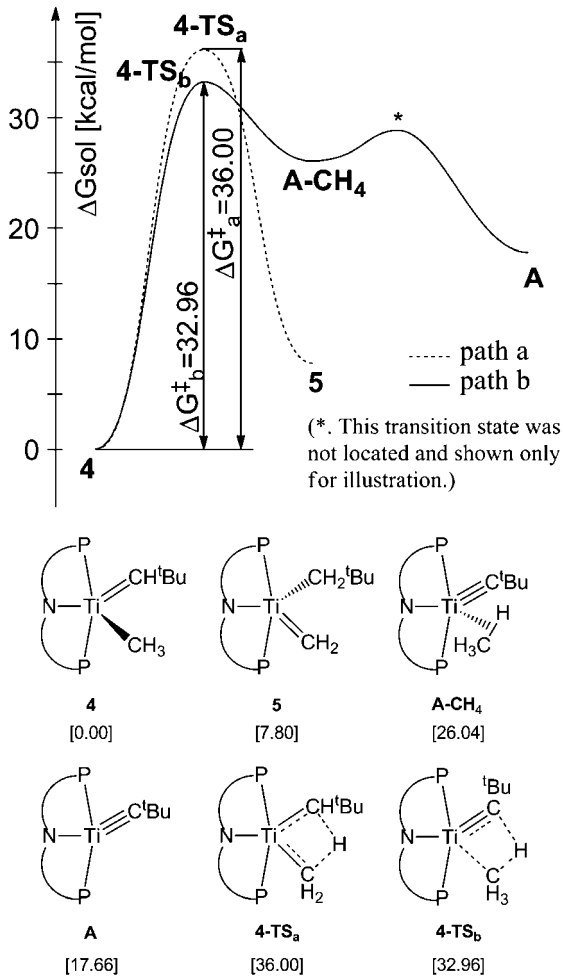


Fig. 4 Computed reaction profile illustrating the competition between methane extrusion (path b) and tautomerization (path a) in complex **4**. Values shown in brackets are computed solution-state free energies (ΔG_{sol}) in kcal mol^{-1}.

indicate an extremely weak α-agostic interaction of the methylidene with the Ti(IV) center. These structural alterations obtained for the optimized geometry computed for **5**, are much less pronounced than those observed in stable tungsten and molybdenum methylidene complexes,[21] in which more acute M–C–H angles are observed (105–107°). Thus, the data presented here suggests that the α-agostic bond in the titanium-methylidene

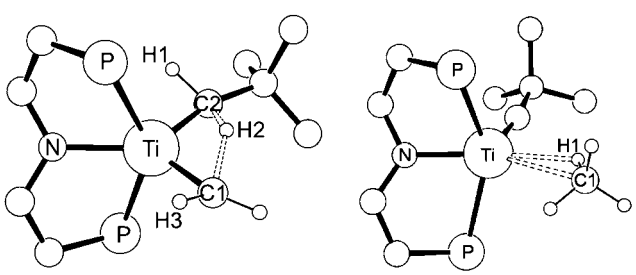


Fig. 5 Computed structures of **4-TS$_a$** (left) and intermediate **A-CH$_4$**. Only the most important atoms are shown for clarity (PNP ligand peripherals are omitted).

complex **5** might be playing a minor role. Presently, we do not know what other factors could be accounting for this difference in energy. To better understand why **5** is energetically difficult to generate, we investigated **4-TS$_a$**. Fig. 5 shows the computed structure of **4-TS$_a$**, which adopts a trigonal-bipyramidal geometry with the migrating hydrogen H1 being located halfway between the donor carbon C1 and the acceptor carbon C2 with C–H distances of 1.51 and 1.50 Å, respectively. Interestingly, in **4-TS$_a$** both C1–H3 and C2–H1 bonds display an α-agostic interaction with the titanium center ($d_{Ti–H3} = 2.21$, $\angle_{Ti–C1–H3} = 90.6°$, $d_{Ti–H1} = 2.09$ Å, $\angle_{Ti–C1–H3} = 83.6°$) lowering the energy of this transition state.[22] This step can be described as a metal mediated α-hydrogen migration as indicated by the relatively short Ti–H2 distance of 1.72 Å, a Wiberg bond order of 0.18 and Natural Population Analysis (NPA) electron density of 0.71 at H2 in the transition state.

As shown in Fig. 4, a conceivable pathway for observed hydrogen exchange in **4** is by way of the alkane sigma-complex, **A-CH$_4$**. In contrast to the relatively long-lived [(2,6-(^{t}Bu$_2$PO)$_2$C$_5$H$_3$N)Rh(CH$_4$)]$^+$ σ-methane complex,[23] **B-CH$_4$**, which was recently characterized in solution by Brookhart and Goldberg, **A-CH$_4$** must be an extremely labile σ-adduct lying 26 and 10 kcal mol^{-1} higher in energy than complex **4** and the separated products, respectively.[23] In **A-CH$_4$** methane occupies one of the equatorial positions of the approximately trigonal-bipyramidal geometry and binds in an η^2-C–H fashion resulting in a slightly elongated C1–H1 bond distance of 1.11 Å (Fig. 5) compared to the C–H distance of ~1.14 Å in **B-CH$_4$**. The calculated Ti–H1 and Ti–C1 distances of 2.26 and 2.85 Å are significantly longer than those found in **B-CH$_4$** ($d_{Rh–H} = 1.87$ Å and $d_{Rh–C} = 2.38$ Å). These longer C–H bonds are in line with the thermodynamics which suggest that methane is very loosely bound in **A-CH$_4$**. The calculated enthalpy difference of 0.8 kcal mol^{-1} between the separated products and **A-CH$_4$** indicates that the methane extrusion step is almost entirely entropy driven[24] and the upper limit of the corresponding barrier can be estimated to be 3–4 kcal mol^{-1}. Intuitively, the rapid, entropy-assisted loss of methane from **A-CH$_4$** to yield **A**[25] should prevent the reactivation of the C–H bond. At present however, our isotopic labeling and kinetic data cannot distinguish either pathway for exchange.

Conclusions

In conclusion, two new paradigms involving metal-carbon multiple bonds have been established. First, we demonstrated that a titanium-carbon triple bond is unambiguously involved in the direct activation of methane at room temperature. Second, we showed indirectly that the methyl hydrogens in **4** are undergoing slow exchange with the alkylidene hydrogen.

The dehydrogenation of CH_4 to methylidene is especially important because it could allow for the conversion of methane to an industrially important reagent such as ethylene, *via* intermolecular "CH_2" coupling routes.[27] However, at present, this conversion has been proposed for silica-supported Ta(III) alkane metathesis catalysts or metal clusters.[4,7,8] The former reaction has been predicted to occur by a series of steps such as σ-bond metathesis of (surface)Ta(H) with methane followed by α-hydride elimination to yield (surface)Ta=CH_2(H).[26] However, our work suggests that 1,2-CH bond addition[9–11] and tautomerization can also be plausible pathways for the dehydrogenation of methane, forming in the process, a terminal titanium methylidene[28] reminiscent of Tebbe's reagent, without necessitating a two-electron redox process.[29] Unfortunately, our labeling and kinetic studies do not provide any evidence for secondary KIE taking place in the exchange process.

The possibility of a σ-methane complex, **A-CH$_4$**, as an intermediate for exchange cannot be discarded, but such a putative species must be relatively long-lived in order to allow for H-exchange rather than replacement with the medium such as benzene. Previous work in our group has established that **A** activates benzene, *via* formation of an adduct **A-C$_6$H$_6$**, which has a long enough lifetime to allow for the determination of the intramolecular equilibrium KIE (C_6H_6/1,3,5-$C_6H_3D_3$, 1.33(3)) which is different from the intermolecular KIE (C_6H_6/C_6D_6, 1.03 (7)).[10a] These results suggest that binding of the arene is the slowest step in the C–H bond breaking process (but not rate-determining overall).

We estimate the rate of exchange in **4** to be slower than, but comparable to the elimination of methane (10^{-6} s^{-1} at 60 °C). The reactivity of **4** with Al(CH_3)$_3$ and NC^{t}Bu suggests this species to be an alkylidyne synthon, **A**. Unfortunately, the latter process is encumbered by the irreversible α-hydrogen abstraction to eliminate methane. Current efforts are being devoted to the other volatile paraffins since β-hydrogens might play an essential role.

Acknowledgements

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